

Ortho and Para Molecules of Water in Electric Field

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Stark effect is calculated by the perturbation theory method separately for the *ortho* and *para* water molecules. At room temperature, a 30%-difference in the energy change is found for the two species put in electric field. This implies a sorting of the *ortho* and *para* water molecules in non-uniform electric fields. The *ortho/para* water separation is suggested to occur in the course of steam sorption on a solid surface and of large-scale atmospheric processes.

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It is a textbook knowledge that an isolated water molecule, H_2O , exists in one of the two forms (spin isomers), *ortho* or *para*, with parallel or antiparallel proton spins, respectively [1]. In the first case a total magnetic moment of the molecule is 1, while in the second case it is 0. Under ambient conditions the gaseous *ortho* and *para* molecules are in a statistical 3:1 equilibrium (further referred as the normal O/P-ratio). In the gas, the *ortho-para* conversion due to collisions and radiation processes is highly improbable [2]. The valuable factor of conversion is magnetic interactions. In the absence of magnetic impurities, the estimated life-time of the gaseous *ortho* and *para* molecules is months [3]. Thus, the water vapor is a true mixture of two gaseous ensembles consisting of magnetic (*ortho*) and nonmagnetic (*para*) molecules. This means that the *ortho* and *para* ensembles can in principle be spatially separated.

For molecular hydrogen, the task of spatial separation of the spin isomers has been solved decades ago [4]. At present, the O/P separation of H_2 is usually attained by catalytically assisted cooling of gaseous H_2 at cryogenic temperatures. Separate existence of *ortho* and *para* water, however, is still questionable. The challenge is to pinpoint those physical properties of the chemically identical *ortho* and *para* water molecules, which can be used for their separation. Here, by the perturbation theory calculations we study response of the *ortho* and *para* water molecules to the dc electric field (Stark effect), and find that these two species have noticeably different electrostatic properties. Although the study of Stark effect in water has a long history [1, 5], the effect, to our knowledge, has never been considered separately for the *ortho* and *para* modifications.

As is generally accepted, we consider a water molecule as a rigid asymmetrical top and choose the coordinate system so that the ξ, η, ζ axes are directed along the three main inertial axes of the molecule [1]. Further we follow a standard procedure described in details in Ref. [6]. The rotational part of Hamiltonian is written as:

$$\hat{H}_{rot} = \frac{\hbar^2}{2} \cdot \left(\frac{\hat{J}_\xi^2}{I_A} + \frac{\hat{J}_\eta^2}{I_B} + \frac{\hat{J}_\zeta^2}{I_C} \right), \quad (1)$$

where $\hat{J}_\xi, \hat{J}_\eta, \hat{J}_\zeta$ are the angular momentum operators, and I_A, I_B, I_C are the main inertial moments of the molecule. The symmetry of the Hamiltonian (1) belongs to the D_2 group, thus the rotational energy levels are classified according to the irreducible representations of this group: A, B_1, B_2 and B_3 . After rotation by π along the ζ direction ($C_\pi(\zeta)$), the wave functions of the A and B_1 symmetries do not change their signs, while the wave functions of the B_2 and B_3 symmetries do.

In the Born-Oppenheimer approximation and neglecting the rotation-vibration interaction, the wave function of water molecule is $|\Psi\rangle = |\psi_s\rangle \cdot |\psi_{el}\rangle \cdot |\psi_{vibr}\rangle \cdot |\psi_{rot}\rangle$, where $|\psi_s\rangle, |\psi_{el}\rangle, |\psi_{vibr}\rangle$, and $|\psi_{rot}\rangle$ are the nuclear spin, electronic, vibrational, and rotational wave functions. According to the Pauli principle, the total Ψ -function should change its sign after permutation of the hydrogen atoms. This permutation is equivalent to the $C_\pi(\zeta)$ rotation. The functions $|\psi_{el}\rangle$ and $|\psi_{vibr}\rangle$ of the ground state are symmetric with respect to $C_\pi(\zeta)$. Whether or not $|\psi_{rot}\rangle$ and $|\psi_s\rangle$ change their signs, depends on in which states, *ortho* or *para*, the water molecule is. Obviously, for the case of the parallel proton spins (the *ortho* molecule) the exchange of the protons does not reverse $|\psi_s\rangle$. In this case, only $|\psi_{rot}\rangle$ is responsible for the sign inversion of the total Ψ -function. Therefore, $|\psi_{rot}\rangle$ of the *ortho* molecule has either B_2 or B_3 symmetries. In contrast, $|\psi_s\rangle$ of the *para* molecule does change the sign when the protons (with antiparallel spins) are interchanged. In turn, $|\psi_{rot}\rangle$ remains sign-constant. Hence, the *para* rotational states have wave functions of the A and B_1 types.

We calculate the rotational levels and corresponding wave functions $|\psi_{rot}\rangle$ using the perturbation theory method. The electric field is assumed to be weak enough so that the level shifts caused by the field are much smaller than the nominal distances between the levels. The direction of the z -axis of the immovable laboratory coordinate system (x, y, z) is chosen along the electric field vector. The interaction energy of the water molecule with electric field is:

$$V = -\mathcal{E} \cdot d_z, \quad (2)$$

where d_z is the projection of the dipole moment of the

water molecule to the z -axis. In the first approximation, the shifts of the levels are determined by the diagonal matrix elements of the operator (2). However, they are equal to zero for the asymmetrical rotators. Thus, the level splitting of the water molecule is a second order effect relative to the electric field:

$$\Delta E_{JM_J n} = \mathcal{E}^2 \sum_{J' M_{J'} n'} \frac{|D|^2}{E_{Jn} - E_{J'n'}}, \quad (3)$$

where $D = \langle J' M_{J'} n' | d_z | J M_J n \rangle$ is a matrix element of d_z , J is a total moment of the molecule, M_J is its projection to the z -axis, the index n numerates different states with given J and M_J . The rotational wave function of the asymmetrical rotator is $|J M_J n\rangle = \sum_k C_k^{(Jn)} |J M_J k\rangle$, where $|J M_J k\rangle$ are eigenfunctions of the operators \hat{J}^2 , \hat{J}_z , and \hat{J}_ξ , with eigenvalues, correspondingly, $J(J+1)$, $M_J = J, J-1, \dots, -J$, and $k = J, J-1, \dots, -J$. Then D can be expressed in terms of the eigen dipole moment of the molecule, $d^{(0)}$, directed along the ζ axis, in a following way:

$$D = \sum_{kk'} C_{k'}^{(J'n')*} C_k^{(Jn)} \langle J' M_{J'} k' | d_z | J M_J k \rangle = d^{(0)} \cdot \sum_{kk'} C_{k'}^{(J'n')*} C_k^{(Jn)} (i)^{J-J'} (-1)^{k-M_{J'}} \times \sqrt{(2J+1)(2J'+1)} \cdot \begin{pmatrix} J' & J & 1 \\ -k & k & 0 \end{pmatrix} \times \begin{pmatrix} J' & J & 1 \\ -M_{J'} & M_J & 0 \end{pmatrix} \cdot \delta_{kk'} \delta_{M_J M_{J'}}, \quad (4)$$

where $\begin{pmatrix} J' & J & 1 \\ -k & k & 0 \end{pmatrix}$ and $\begin{pmatrix} J' & J & 1 \\ -M_{J'} & M_J & 0 \end{pmatrix}$ are the Klebsh-Gordon coefficients which are non-zero only for $J' = J$ and $J' = J \pm 1$. In view of expression (4), the general formula (3) is reduced to:

$$\Delta E_{JM_J n} = -\frac{1}{2} \mathcal{E}^2 \left(\alpha_{Jn} + 2\beta_{Jn} \left(M_J^2 - \frac{1}{3} J(J+1) \right) \right), \quad (5)$$

where α_{Jn} is the total shift of the "center of gravity" of the split level and β_{Jn} is the shift of the sub-levels relative to this "center of gravity". From Eqs. (3) and (5), by performing summation over M_J and $M_{J'}$, we obtain the expressions for α_{Jn} and β_{Jn} . The Stark behavior of the rotational levels of the water molecule is then calculated with the following parameters [7, 9]: $a = \hbar^2/I_A = 55.7 \text{ cm}^{-1}$, $b = \hbar^2/I_B = 18.6 \text{ cm}^{-1}$, $c = \hbar^2/I_C = 29.0 \text{ cm}^{-1}$, and $d^{(0)} = 1.84 \text{ Debye}$.

The results of the calculations for $J = 0; 1$ are shown in Fig. 1. The calculations are limited by the field of 10^6 V/cm to meet the requirements of the second order approximation method we used. It is seen from the Figure, that the singlet *para*-level $|0A\rangle$ with $J = 0$, shifts

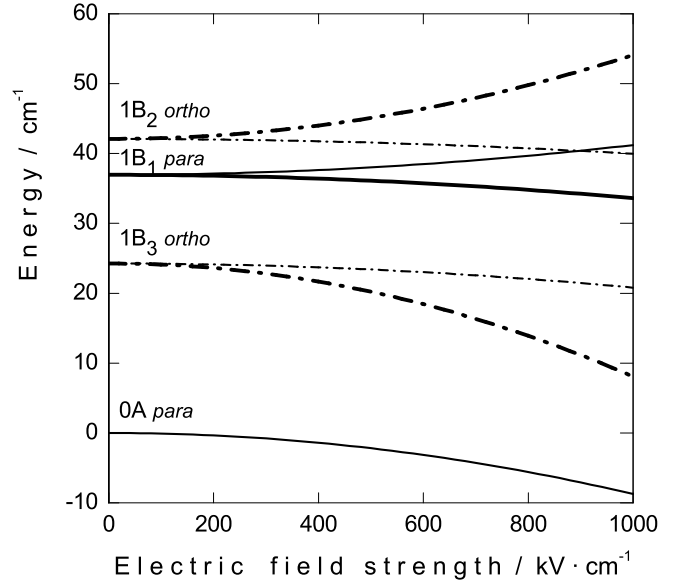


FIG. 1: Stark effect for the water molecule: positions of the lowest four rotational energy levels, E_J , in external electric field. Light and bold lines show non-degenerated and twice degenerated levels, correspondingly.

down when the field is applied. This is, of course, in accordance with the general quantum mechanical theorem [6]. The levels with $J = 1$ split into 2 sub-levels. One of these two sub-levels has $M_J = 0$ and is not degenerated (thin lines in Fig. 1). Another sub-levels correspond to $M_J = \pm 1$ and are twice degenerated (bold lines).

Fig. 1 reveals qualitatively different trends for the *ortho* and *para* levels in the field. When the field increases, the majority of the *para*-levels (the singlet $|0A\rangle$ and the twice-degenerated sub-level $|1B_1\rangle$) goes down. Only one of the *para* levels goes up. Thus, the net energy shift of the *para* levels is appreciably negative. In the case of *ortho* molecules, the twice-degenerated *ortho* levels (bold dash-dotted lines) diverge symmetrically as field goes up, the non-degenerated *ortho* levels lowering slightly only. As a result, the net energy shift of the *ortho* levels is notably, approximately two times, smaller than the net shift of the *para* levels.

Taking into account the Boltzmann distribution of water molecules over the energy levels, one can write the net energy shifts $\overline{\Delta E_O}$ and $\overline{\Delta E_P}$ of the gaseous *ortho* and *para* molecules in the electric field \mathcal{E} :

$$\overline{\Delta E_{O,P}} = -\frac{1}{2} \mathcal{E}^2 \frac{\sum \alpha_{Jn} (2J+1) \exp(-\Delta E_{JM_J n}/T)}{\sum (2J+1) \exp(-\Delta E_{JM_J n}/T)}, \quad (6)$$

where $\Delta E_{JM_J n} = E_{JM_J n} - E_0$ are the energies of the *ortho* and *para* levels E_J about the energy E_0 of the lowest $|1B_3\rangle$ and $|0A\rangle$ levels, correspondingly; T is the temperature; the summation is carried out separately over the *ortho* and *para* levels.

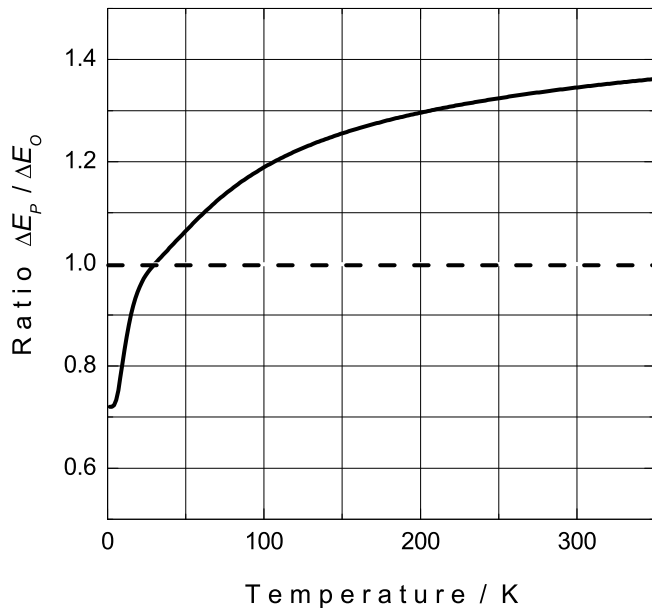


FIG. 2: Ratio of the energy Stark shifts for the *para* and *ortho* water molecules as a function of temperature. The dashed line notices the unity for eye.

The ratio $R = \overline{\Delta E_P} / \overline{\Delta E_O}$ gives a comparative response of the *ortho* and *para* water molecules to an external electric field. R can be considered as a ratio of the forces acting on the *para* and *ortho* water molecules in a non-uniform electric field. As is seen from Eq. 6, it is a function of temperature T and does not depend on the field strength.

We have calculated $R(T)$ for 16 lowest rotational levels ($J \leq 3$), laying in the range of 0-283 cm^{-1} and containing a 70 % deal of the molecules at room temperature. The Stark shifts of the higher levels of the asymmetric top decrease quickly when J increases [1], therefore the contribution of the higher energy levels in $R(T)$ is comparatively small (less of 5% at room temperature). The result of our calculations is presented in Fig. 2.

The drop of the $R(T)$ at $T < 30$ K is easy to understand from simple considerations. Indeed, at low temperatures the water molecules occupy mainly the two lowest *ortho* $|1B_3\rangle$ and *para* $|0A\rangle$ levels. In accordance with Fig. 1, the *ortho* $|1B_3\rangle$ level is of a superior "Stark flexibility". In an electric field it goes sharply down predominantly causing the greater energy lowering of the *ortho* molecules.

At elevated temperatures the additional *para* and *ortho* levels get filled with molecules resulting in levelling off of the total energy Stark shifts of the *ortho* and the *para* molecules. Surprisingly, however, the $R(T)$ ratio does not go to the unity, but exceeds it, reaching the 1.34 value at room temperature. This implies that the *para* molecules in non-uniform electric fields experience a one third stronger electric force than the *ortho* molecules.

The *para* molecules are thus proved to be more active as the "high field seeking" molecules.

One can suggest the occurrence of the O/P sorting effect for the *ortho* and *para* water molecules in non-uniform electric fields, as it is typically happening with polar molecules [7]. Let us note, it is just electric rather than magnetic field that leads to a sizable distinction between the molecules with different magnetic arrangement.

Obviously, one of the fields where the distinction between electrostatic properties of the *ortho* and *para* water molecules can naturally be revealed is a water vapor sorption on a solid surface. The impinging water molecules are unavoidably exposed to the non-uniform surface electric field and, therefore, are suggested to undergo the O/P separation effect. A rough estimate [1] of the total rotational energy drop Δ of the water molecule on the surface is: $\Delta \sim -d \cdot \mathcal{E} \sim -1$ kJ/mol, where $d = 1.84$ Debye is a dipole moment of water molecule and $\mathcal{E} \sim 10^6$ V/cm is taken as an estimate of both, a typical surface electric field and the highest strength allowed by our perturbation method. As is seen, the dipole attraction energy is not negligible in comparison with the real physadsorption energies of 5 - 20 kJ/mol [8]. The 30% difference in Δ for the *ortho* and *para* molecules looks large enough to be detectable during the adsorption. We suggest that this effect is responsible for the O/P water separation observed in absorption experiments with water vapor [9].

Beyond the sorption, a sizable effect of the O/P water separation can be suggested to occur in the atmosphere. In fact, the water vapor and atmospheric electricity (ranging from 100 V/m to 1000 V/m normally and to millions V/m in lightnings) are inherent attributes of the atmosphere. Allowance of O/P water separation may give a new insight to the atmospheric phenomena.

Summarizing, our calculations point to a remarkable difference in the forces acting on the *ortho* and *para* water molecules subjected to non-uniform electric field. This distinction is of a fundamental origin. Therefore, we suggest it should play an important role in nature environments.

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